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Eu^{III} functionalized silica nanoparticles encapsulating chiral Cr^{III} complexes with simultaneous unpolarized red and polarized NIR-I luminescence

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Supporting Information

(20 pages)

Appendix. Experimental section.

Solvents and starting materials

All the chemicals were purchased from commercial suppliers and used without further purification. The $Cr(CF_3SO_3)_2 \cdot 2H_2O$ and the ligand dqp = 2,6-di(quinolin-8-yl)pyridine were prepared according to the published method.[S1-S2]

Synthesis

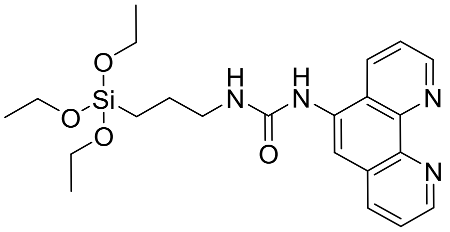
Preparation of the enantiopure Cr(III) complexes

The complex *rac*-$[Cr(dqp)_2](SO_3CF_3)_3$ was prepared according to the reported procedure.[S3] Enantiopure materials were obtained by chiral stationary phase HPLC resolution on an Shimadzu LC-20AR (quaternary pump, auto sampler, column thermostat and diode array detector) using a semi-preparative CHIRALPAK® IC column (250 x 10 mm, 5 µm) with a eluent optimized composition of DCM/EtOH/TEA/TFA (49.5/49.7/0.5/0.3 v/v/v/v) and HPLC grade solvents. The samples were prepared in 100% ethanol and the optimized conditions were 4.5 mL/min and 35°C. Analytical runs after the separation were run in an analytical CHIRALPAK® IC/250 x 4.6mm, 5µm (see fig. S1). Salt metathesis of the eluted fractions with KPF_6 finally led to the isolation of the two enantiomers ($\lambda\lambda/\delta\delta$)-$[Cr(dqp)_2](PF_6)_3$ in similar proportions. Elemental analysis for the two enantiomers: first eluted fraction: $C_{46}H_{30}CrF_{18}N_6P_3 \cdot 2H_2O$ %, found: C: 46.01, N: 7.1, H: 3.1; calculated: C: 46.44, N: 7.06, H: 2.88; second eluted fraction: $C_{46}H_{30}CrF_{18}N_6P_3 \cdot 2H_2O$ %, found: C: 46.21, N: 6.9, H: 3.2; calculated: C: 46.44, N: 7.06, H: 2.88

In order to substitute the hexaflurorophosphate anions by chlorines, anion exchange using a saturated acetone solution containing tetrabutylammonium chlorine was achieved. The resulting ($\lambda\lambda/\delta\delta$)-$[Cr(dqp)_2](Cl)_3$ complexes were highly soluble in water as desired for the synthesis of the functionalized SiO_2 nanoparticles.

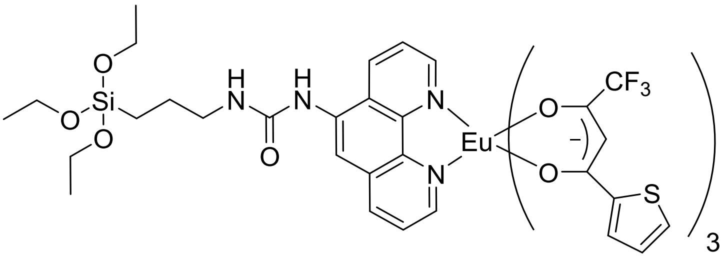
Synthesis of the ligand 1-(1,10-phenanthroline-5-yl)-3-(3-(triethoxysilyl)propyl)urea (phen-Si)

5-amino-1,10-phenanthroline (0.82 mmol, 160 mg) was dissolved in $CHCl_3$ (15 mL), and 3-(triethoxysilyl)propyl isocyanate (0.9 mmol, 0.22 mL) was added to the solution. The mixture was then reduced to a volume of 1 mL and refluxed at 75 °C under Ar overnight. The reaction mixture was cold down to room temperature and hexane was added to precipitate a white powder. The crude product was purified by column chromatography (SiO_2: CH_2Cl_2/MeOH (0-2%) to give the pure product (Yield: 80%). ^{1}H-NMR (400 MHz; $CDCl_3$) 0.65 (2H, m), 1.11 (9H, t), 1.70 (2H, m), 3.35 (2H, m), 3.75 (6H, q), 6.34 (1H, br), 7.20 (1H, dd), 7.57 (1H, dd), 8.15 (1H, m), 8.18 (1H, br), 8.37 (1H, m), 8.38 (1H, s_{br}), 8.86 (1H, m), 9.00 (1H, m).



Synthesis of the complex Eu(tta)$_3$(phen-Si)

2-Thenoyltrifluoroacetone (TTA) (0.67 mmol, 0.150 mg) was dissolved in 5 mL of absolute ethanol, and triethylamine (94 μL) was added. After 10 min of stirring, the ligand (Phen-Si) (0.22 mmol, 0.096 g) was added, followed by $Eu(NO_3)_3 \cdot 6H_2O$ (0.22 mmol, 0.1 g). The reaction mixture was heated at 50–60 °C and stirred under Ar for an appropriate time (1.5 h). A yellow solution was obtained. After filtering with PTFE membrane twice, the solvent was evacuated and the residue dried until obtaining a powder (45%). Elemental analysis for $C_{46}H_{45}N_4O_{10}F_9S_3SiEu$, %, found: C: 44.01, N: 4.71, H: 3.2; calculated: C: 43.81, N:4.44, H: 3.7.



Surface functionalization of Cr@SiO$_2$NPs with the luminescent europium complex (*λλ*/*δδ*-EuCr@SiO$_2$NPs)

10 mg of *λλ*-Cr@SiO_2NPs and *δδ*-Cr@SiO_2NPs were suspended in a solution containing 20 mg of the Eu(tta)$_3$(phen-Si) dissolved in 1 mL of a mixture CH_2Cl_2 and heated to 35 °C for 48 h. After this time, the nanoparticles were recovered by centrifugation and washed successively with ethanol and acetone until the luminescence signal of the europium complex was not observed in the washings' solvents. Finally, the nanoparticles were dried at 50 °C for 16 h.

Experimental part

Nanoparticles were characterized by transmission electron microscopy (TEM) using a LIBRA 120 PLUS Carl Zeiss electron microscope operating at 200 keV and scanning electron microscopy (SEM) using a HITACHI S-510. 5 mg of the material were redispersed by sonication (30 min) in 1 mL of EtOH. Carbon reinforced copper grids (200 mesh) were submerged into suspension 50 times and then allowed to dry in air for at least 48 h. The size of the particles was determined by ''manual counting'' using ScionImage software (http://www.scioncorp.com). High-Angle Annular Dark-Field (HAADF)-STEM images and EDX analyses were recorded on a HAADF FEI TITAN G2 instrument working at an accelerating voltage of 200 kV in the scanning mode with a probe diameter of 0.5 nm. Elemental analyses were carried out on a Fisons-Carlo Erba analyser model EA 1108. X-ray photoelectron spectroscopy (XPS) experiments were carried out in a Kratos Axis Ultra-DLD. Inductive Coupled Plasma (ICP) emission spectroscopy was carried out in a ICP-OES Perkin-Elmer optima 8300. Emission and excitation spectra were measured on a UV-VIS-PTI QuantaMaster™ 8000 spectrofluorometer equipped with a Picosecond Photon Detector (230-850nm, PPD-850, HORIBA Scientific) and a continuous Xenon Short Arc Lamp (190-2000nm, USHIO). All the spectra (emission and excitation) were corrected with Real-time corrections function. TCSPC lifetime measurements were performed using a 375 nm excitation wavelength provided by a flash lamp light source (1 μs pulse, HORIBA Scientific). Low temperature (77 K) was achieved using liquid quartz transparent Deward filled with liquid N_2 in the centre of which samples were placed. Samples solutions (H_2O/DMSO) 5/5, were introduced in quartz tube (4 mm interior diameter) and introduced into the sample holder of the Dewar. All emission quantum yields were measured according to an absolute method which makes use of an integration sphere. Electronic circular dichroism (ECD) spectra were recorded on a Jasco J-815 spectropolarimeter at 20 °C in a 1 cm cuvette. The ECD spectra showed in this work are an average spectrum calculated after 3 scans (each one). For ECD measurements a fixed 0.1 s of integration time was selected. The Circularly Polarized Luminescence (CPL) were recorded with an Olis DSM172 spectrophotometer. The spectra were recorded at approximately 10^{-5} M concentrations in HPLC grade solvents and room temperature. A fixed wavelength of 370 nm provided by a LED source was used, 1.0 s of integration time was selected, the CPL spectra showed in this work correspond to average spectra calculated after 10 scans. To study the possible leaching of the encapsulated Cr(III) complexes into nanoparticles, a dialysis membrane charged with a water suspension of the ***rac*-Cr@SiO$_2$NPs** was sealed and introduced in a water solution. The mixture was stirred for several weeks, and the absorption spectra of the outer water solution was recorded periodically.

Theoretical studies

The Orca[S4] (version 5.0.2) software package was used to investigate the structural and electronic properties of $[Cr(dqp)_2]^{3+}$. Starting from the X-ray diffraction structure, the geometry of the ground $^4A_2$ state was obtained from DFT optimizations using the unrestricted version of the Becke three-parameters exchange function in combination with the Lee-Yang-Parr correlation functional (UB3LYP). The Ahlrichs' polarized valence triple-ζ basis set def2-TZVPP was used for these optimizations. The D3 version of Grimme's dispersion with Becke-Johnson damping (GD3BJ) was applied. Solvent effects were included via the Conductor-like Polarizable Continuum Model (CPCM) as implemented in Orca 5.0.2 with the dielectric constant of acetonitrile. Optimized geometries were confirmed to be stationary points by analysis of their vibrational frequencies. Tight convergence criteria were selected for the optimization step. The resolution of identity approach for the Coulomb term in combination with the chain-of-spheres approximation for the exchange term (RIJCOSX) was applied. The zero-order relativistic approximation (ZORA) was used to describe relativistic effects in all calculations. Spin density information was extracted from the optimized geometries.

Ab initio ligand field (AILF) analysis was performed over the optimized geometry using Orca version 5.0.2. The complete-active-space self-consistent field method (CASSCF) together with the fully internally contracted N-electron valence perturbation theory to second order (FIC-NEVPT2) was used, selecting only the 3d orbitals as active space (CASSCF(3,5)/FIC-NEVPT2) and using the def2-TZVPP basis set in combination with the RI-JK approximation (def2/JK as auxiliary base). 10 quartet and 40 doublet roots were computed for the AILF analysis.

Subsequently, the active space was expanded to accurately model the ligand field. Dominant bonding/antibonding orbitals formed between ligand and chromium and a second d shell were considered, creating an active space of 7 electrons and 12 orbitals (CASSCF(7,12)/FIC-NEVPT2). 10 quartet and 9 doublet roots were computed to calculate the energies of the excited states.

Experimental characterization

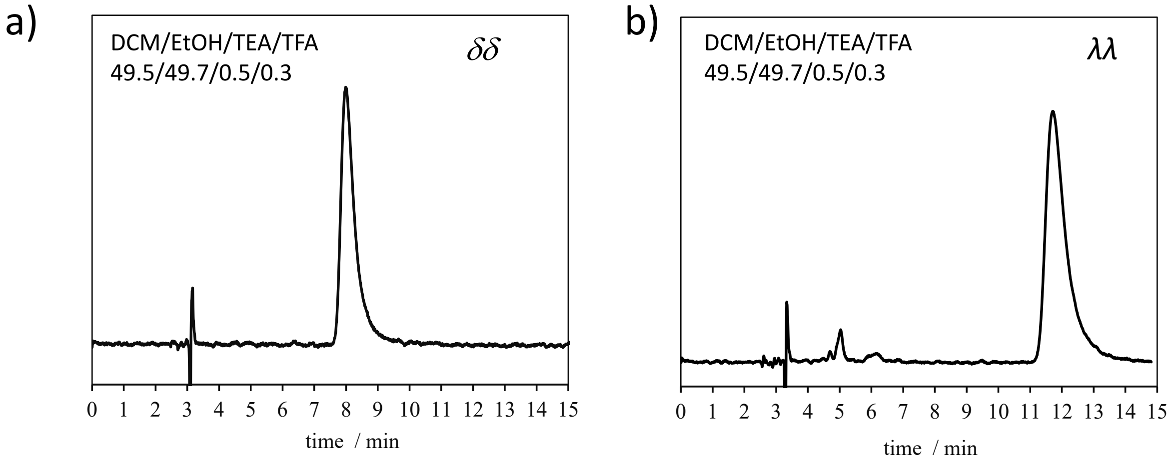


Fig. S1. HPLC traces of the two fractions using a Chiralpak IC, $CH_2Cl_2/CH_3CH_2OH/N(CH_2CH_3)_3/CF_3COOH$ 49.5:49.7:0.5:0.3 (v/v/v/v). UV detection at 363 nm. Tª = 35 ºC.

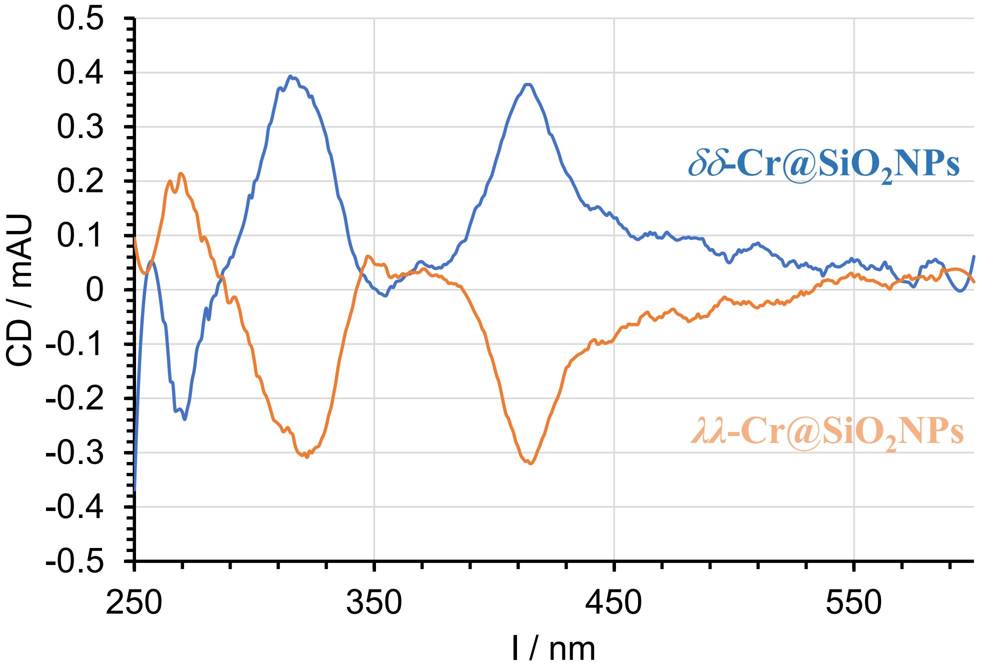
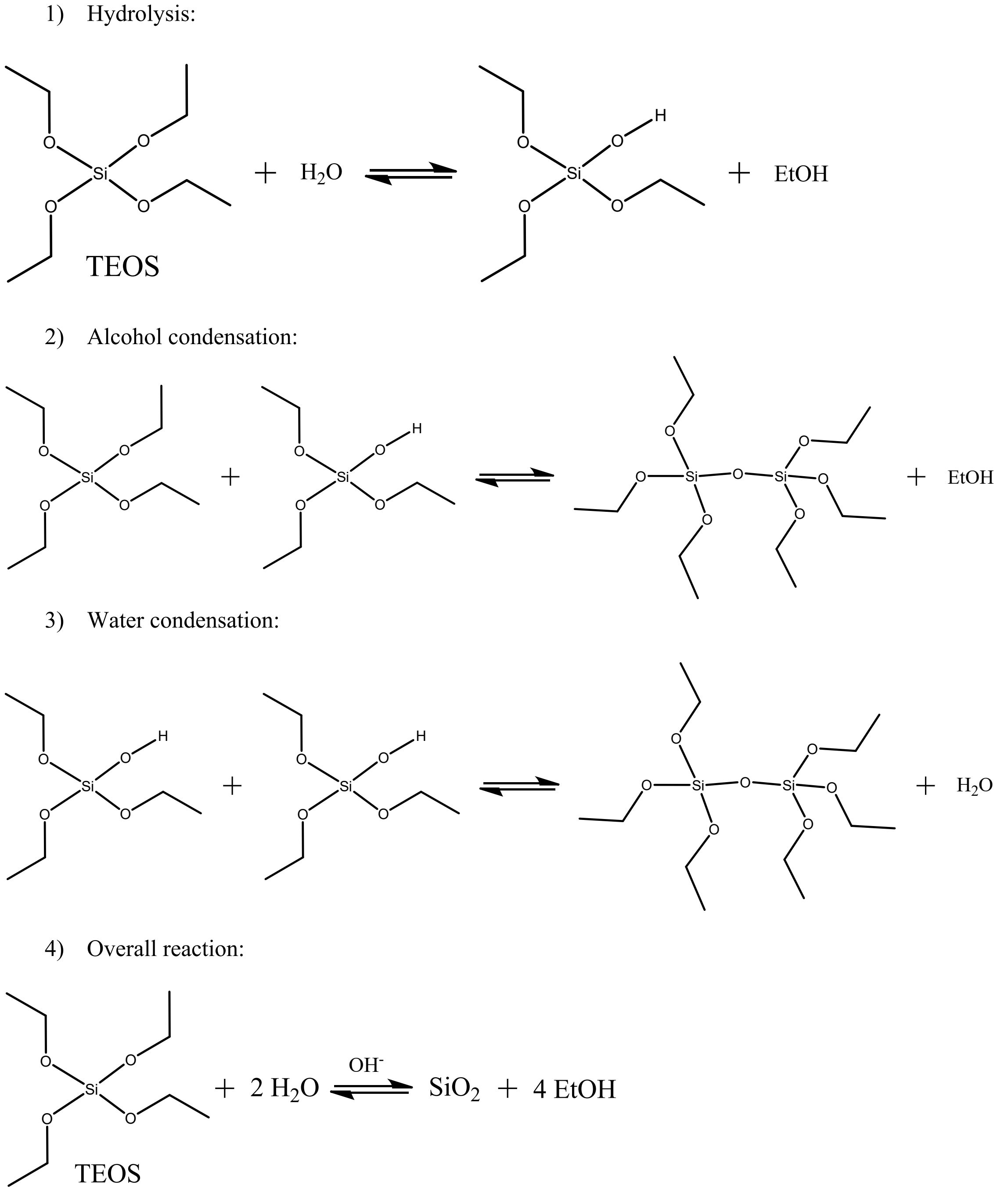


Fig. S2. CD spectra of the of the **λλ-Cr@SiO_2NPs** and **δδ-Cr@SiO_2NPs in ethanol at room temperature**

Scheme 1. Mechanistic formation of the silica matrix.

In this study, the synthesis of the silica nanoparticles starts from the hydrolysis of tetraethyl orthosilicate (TEOS) in a *water in oil* microemulsion. The silica synthesis includes the hydrolysis and condensation (polymerization) of the hydrophilic silica precursor in the presence of a base catalyst (ammonia):



1) Hydrolysis:

2) Alcohol condensation:

3) Water condensation:

4) Overall reaction:

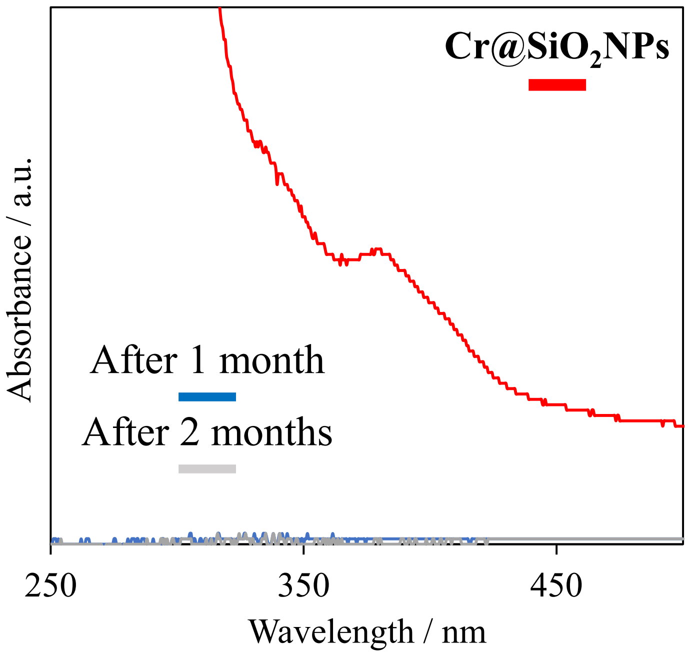


Fig. S3. UV-Vis spectra of the *rac*-Cr@SiO_2NPs (red) and the recovered water solution from the dialysis tests: after 1 month (blue spectrum) and 2 months (grey spectrum).

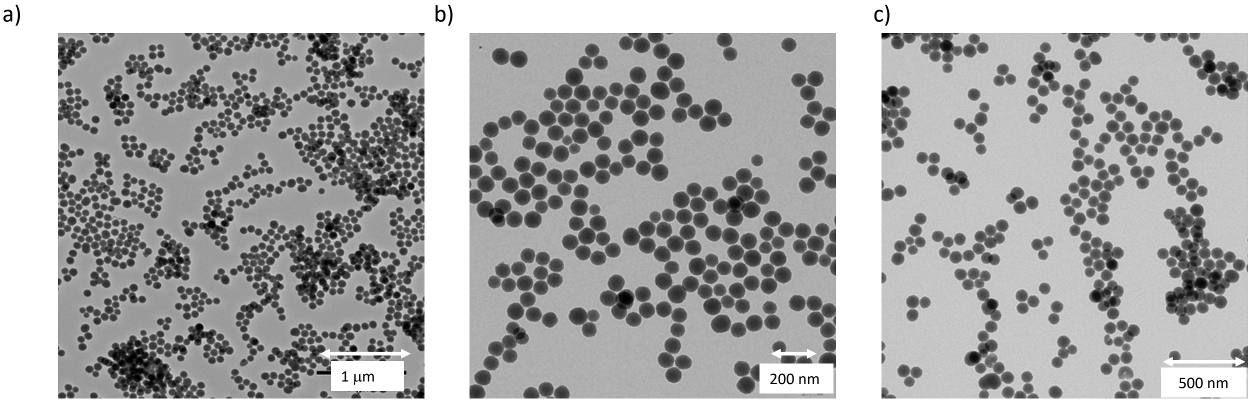


Fig. S4. TEM images of the *rac*-Cr@SiO_2NPs.

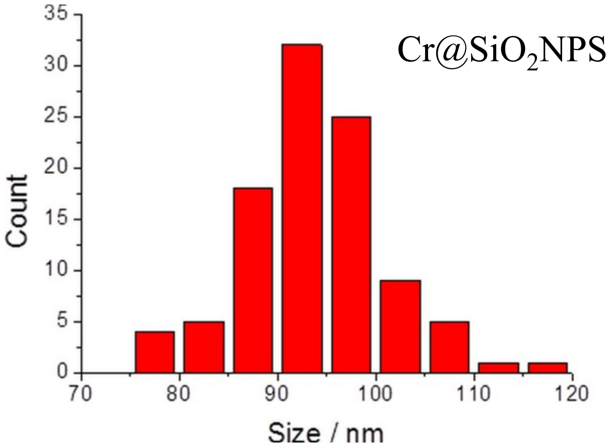


Fig. S5. Size distribution of *rac*-Cr@SiO_2NPs.

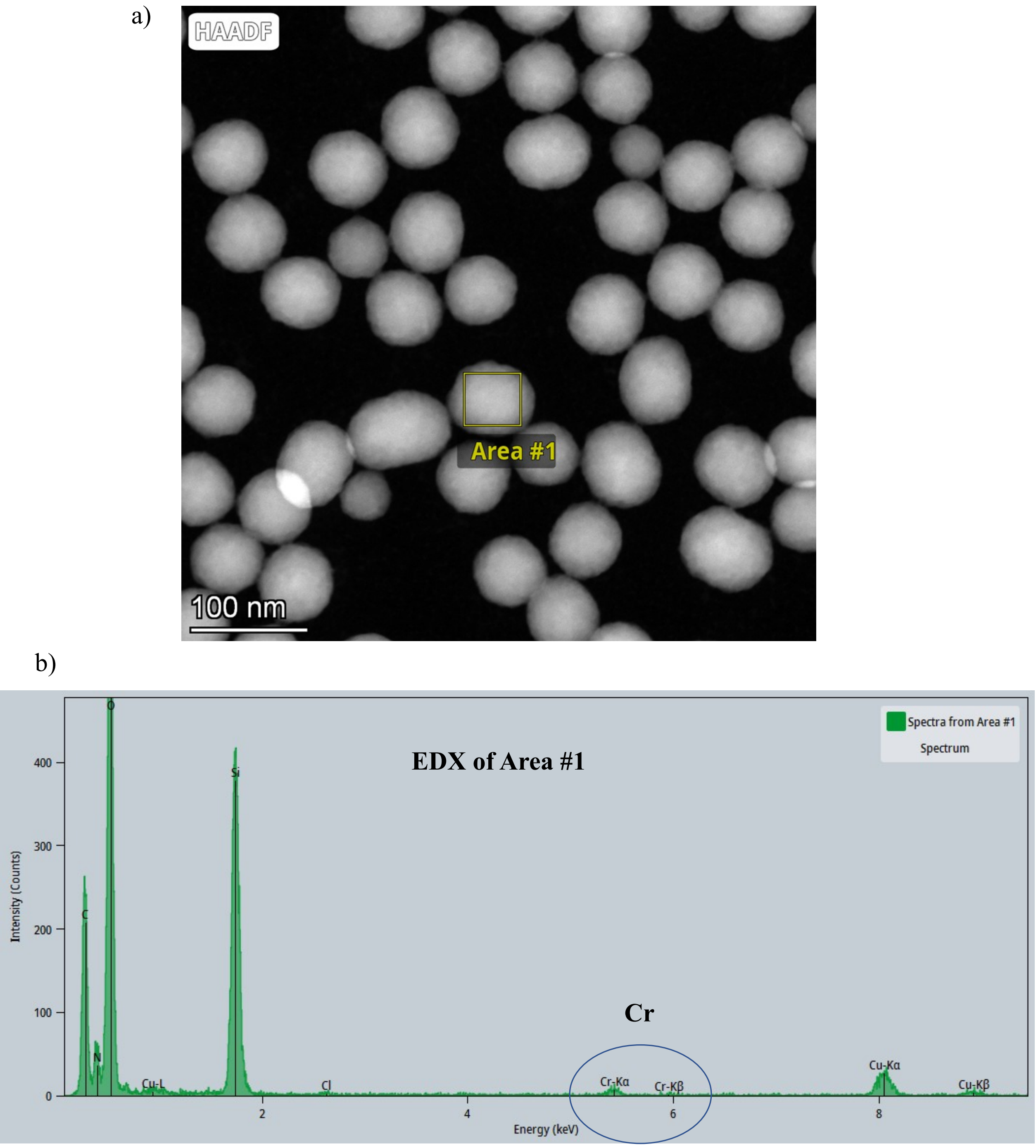


Fig. S6. a) HAADF and b) EDX analysis of λλ-Cr@SiO$_2$NPs.

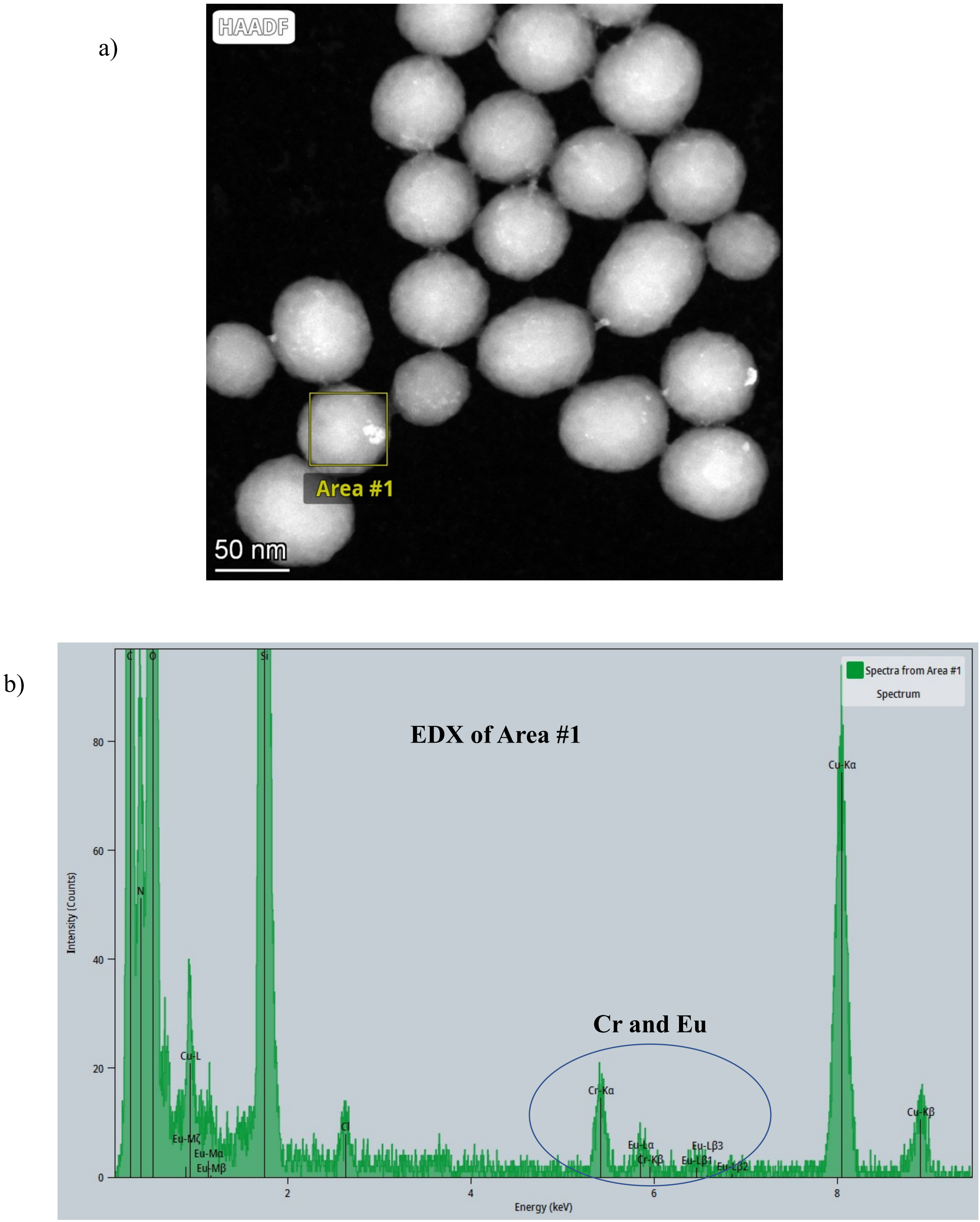


Fig. S7. a) HAADF and b) EDX analysis of λλ-EuCr@SiO_2NPs.

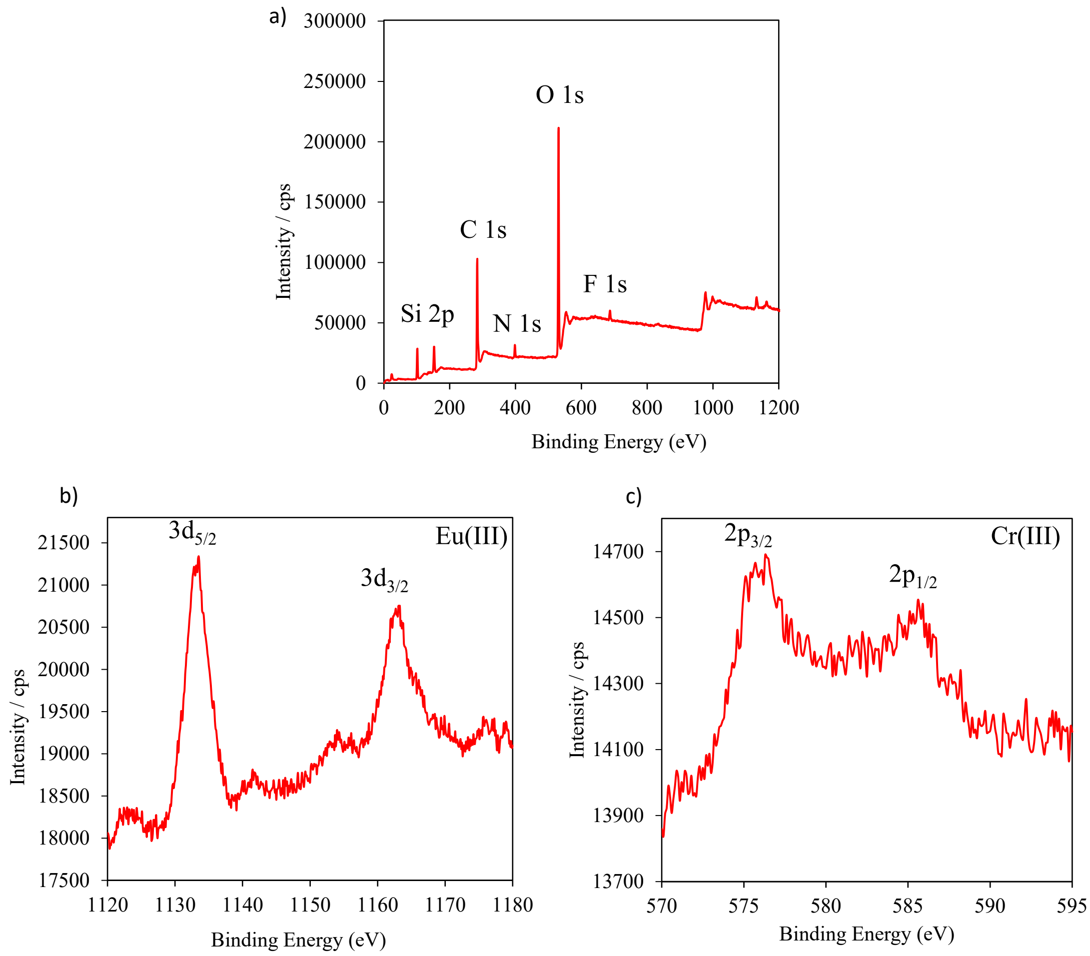


Fig. S8. X-ray photoelectron spectroscopy (XPS) survey spectra of the hybrid EuCr@SiO_2NPs material.

Peak	Type	Atomic Conc %	Mass Conc %
C	1s	48.85	30.32
O	1s	33.49	27.69
N	1s	2.99	2.16
Si	2p	9.78	14.2
F	1s	1.29	1.27
Eu	3d	2.85	22.37
Cr	2p	0.74	1.99

Table S1. XPS analysis of elements on the EuCr@SiO_2NPs surface.

Ab initio ligand field analysis

Table S2. AILF parameters computed from CASSCF(3,5)/FIC-NEVPT2.

	B (cm^{-1})	*C* (cm^{-1})	*C/B*
[Cr(dqp)$_2$]$^{3+}$	982	2965	3.02

Complete active space analysis of excited states

Table S3. CASSCF(7,12)/FIC-NEVPT2 results of [Cr(dqp)$_2$]$^{3+}$. Energies in cm^{-1}.

^{2}E (1)	^{2}E (2)	^{2}T$_1$ (1)	^{2}T$_1$ (2)	^{2}T$_1$ (3)	^{2}T$_2$ (1)	^{2}T$_2$ (2)	^{2}T$_2$ (3)	^{4}T$_2$ (1)	^{4}T$_2$ (2)	^{4}T$_2$ (3)
15449	16040	**15069**	15721	16002	23074	23992	24000	22051	23122	23736

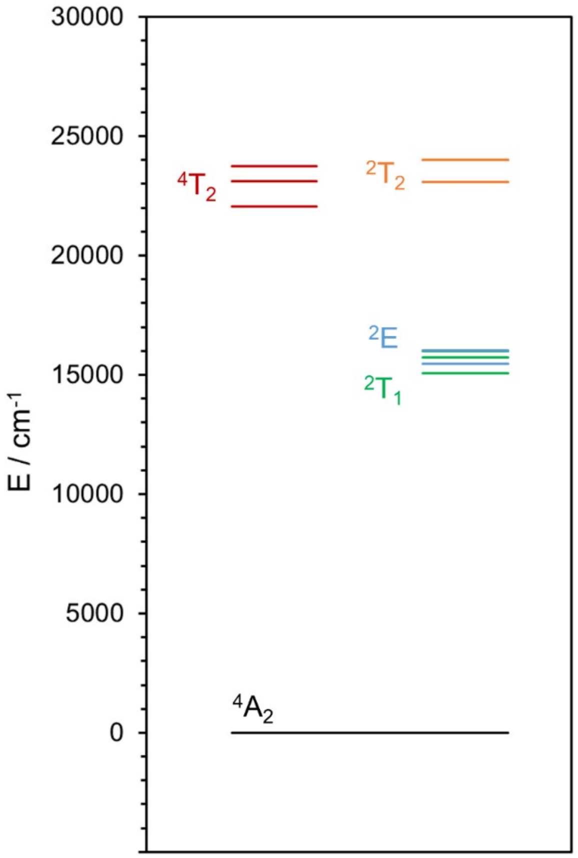
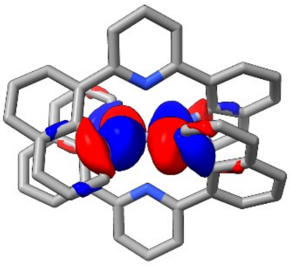
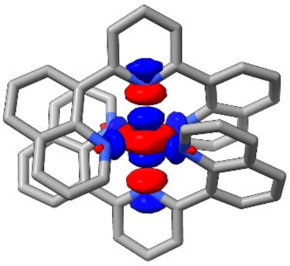
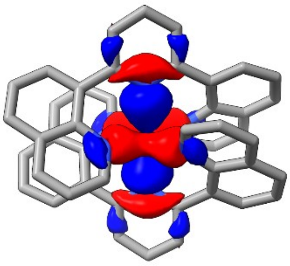
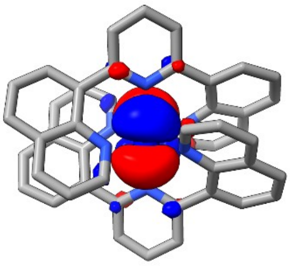
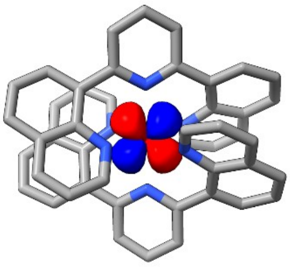
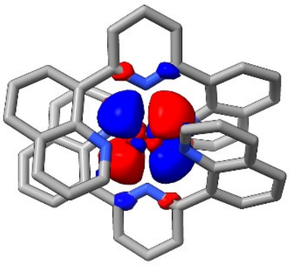
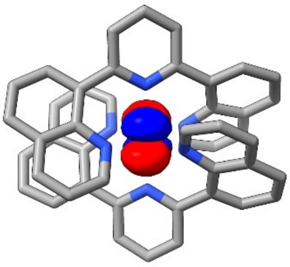
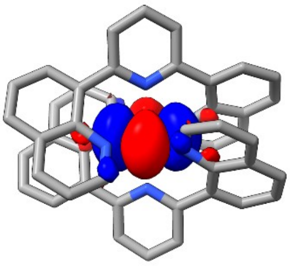
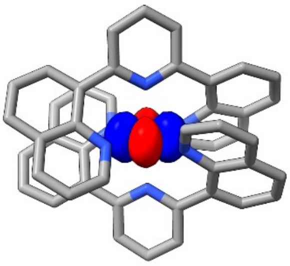
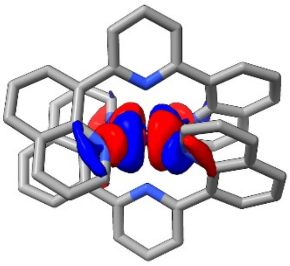
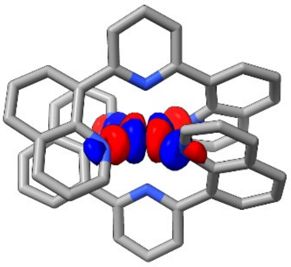
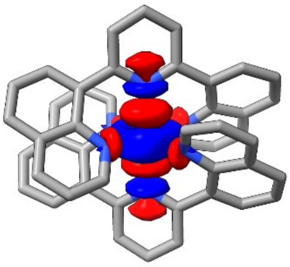


Fig. S9. Schematic representation of the energy levels for the calculated (CASSCF(7,12)/FIC-NEVPT2) excited states of [Cr(dqp)$_2$]$^{3+}$.

Table S4. Orbitals used in the CASSCF(7,12)/FIC-NEVPT2 calculations for $[Cr(dqp)_2]^{3+}$.

#	E (Hartrees)	Orbital	#	E (Hartrees)	Orbital
181	–0.851700		187	–0.178170	
182	–0.851661		188	0.741915	
183	–0.404799		189	0.762311	
184	–0.392601		190	0.741497	
185	–0.392173		191	1.245554	

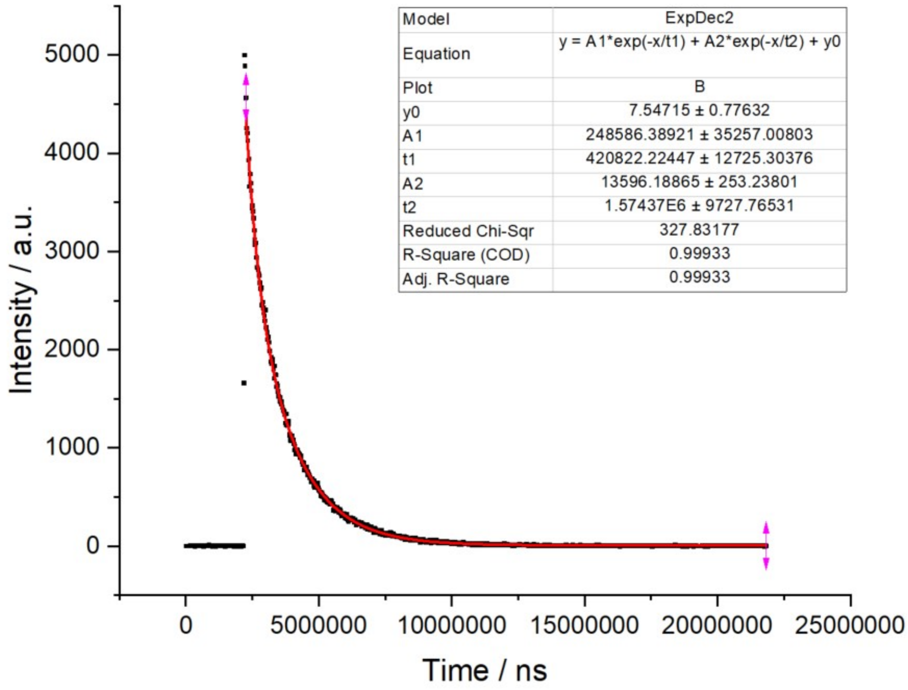
186	–0.194247		192	1.387279	

Geometries

Cr	0.00089290187637	-0.00150948257853	0.00351725232803
N	-1.42233374143264	-0.09879917406190	-1.50281179369531
N	0.00867771004072	-2.04947112321254	0.04320380388330
N	1.42788026163271	-0.02940212136962	1.50932693374992
N	1.42627442480997	0.03829129055149	-1.50380048798978
N	-0.00888832637599	2.04635548046625	-0.03658433765486
N	-1.42234385265307	0.08385954266818	1.51002419369534
C	-1.47767585759928	0.85605896823342	-2.42559913610722
H	-0.57523199657057	1.42471079643559	-2.58946415073319
C	-2.64528721337828	1.17378459213881	-3.12005847832730
H	-2.62492755134900	1.95773040174652	-3.86135590636224
C	-3.80673240336057	0.53504783536581	-2.76927160775790
H	-4.75408391375542	0.81622888538786	-3.20941792524941
C	-3.77750916003725	-0.50703056823050	-1.82051507435538
C	-4.94920274686243	-1.17679475718638	-1.40631228778733
H	-5.90066246556834	-0.85964553254530	-1.81019261806465
C	-4.86418228889124	-2.19777065803327	-0.49845312050956
H	-5.75514979954374	-2.69353812010408	-0.14156577540138
C	-3.60853078068470	-2.64620449419515	-0.06175677149689
H	-3.56965997209718	-3.49810032812375	0.60036610962717
C	-2.42574979702195	-2.04286404324318	-0.45717057735106
C	-2.52117832718004	-0.87789816094771	-1.26615612274513
C	-1.14611261681284	-2.73118802354501	-0.16523978749966

C	-1.14918167097896	-4.12391715158937	-0.16149949696042
H	-2.05801385072988	-4.65796559073361	-0.38400215184288
C	0.01727978796699	-4.81441145598865	0.10259452227141
H	0.02046607387469	-5.89496823647877	0.12613493169881
C	1.17954941793543	-4.10611112969780	0.33610365781168
H	2.09197153316599	-4.62402025858848	0.58104570322261
C	1.16767693719537	-2.71456613316384	0.27965216649965
C	2.44315057913737	-2.00673295434791	0.54107016319814
C	3.62925293793954	-2.61763008916493	0.16836856069334
H	3.59534999844224	-3.49577320792129	-0.45889001764115
C	4.88228588061725	-2.14412102456929	0.58591815921651
H	5.77630391140188	-2.64772700221007	0.24809009354290
C	4.96111929043426	-1.08846907319319	1.45375880547039
H	5.91074205857131	-0.75025455954106	1.84462761966903
C	3.78537802607830	-0.41069820121685	1.84284134408014
C	3.80756828727942	0.66624913201069	2.75198100020557
H	4.75276201797947	0.96986238975389	3.18166344969415
C	2.64192320743074	1.31045611774711	3.07807348230618
H	2.61637462223069	2.12155501915348	3.78939159285351
C	1.47671030542256	0.96019332137390	2.39523527149587
H	0.57088311347092	1.52952087703329	2.53670685827624
C	2.53144971965913	-0.81031516545627	1.30340867981015
C	1.48289275434975	-0.95074414720990	-2.38984503751482
H	0.58153405744116	-1.52711243329305	-2.53151199078030
C	2.65084308119613	-1.29175009049727	-3.07270351214241
H	2.63172345703371	-2.10294286500015	-3.78411735417895
C	3.81140549117947	-0.63843740445688	-2.74651314124540
H	4.75895932574942	-0.93457962698236	-3.17621844269044
C	3.78070639892576	0.43826666010440	-1.83732531299393
C	4.95092869592234	1.12560649621131	-1.44835043523406
H	5.90327140500597	0.79492607662713	-1.83907151923247
C	4.86355424930422	2.18093790429035	-0.58092243202041

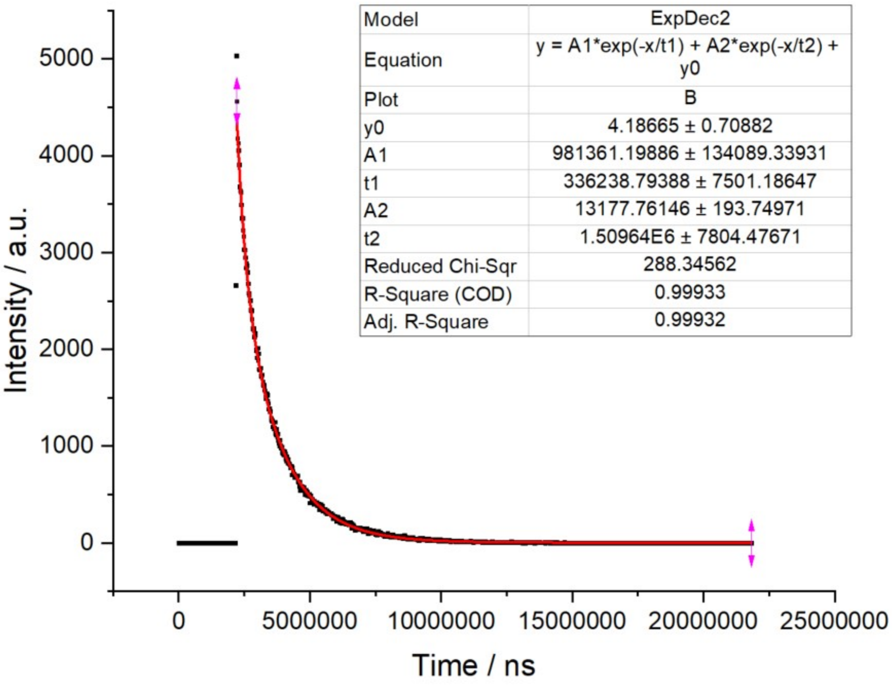
H	5.75347152598166	2.69199480272488	-0.24344828512761
C	3.60675058437069	2.64433359913874	-0.16330796711245
H	3.56564038116029	3.52236119324599	0.46369955133469
C	2.42567789362018	2.02357170863126	-0.53567004487790
C	2.52363813537372	0.82788569561137	-1.29794985364001
C	1.14435662758319	2.72092815528566	-0.27441662365780
C	1.14449769264793	4.11242348817161	-0.33258737495383
H	2.05243963316776	4.63766038327236	-0.57857187642574
C	-0.02357241020456	4.81120563687540	-0.09924879609116
H	-0.02953300919946	5.89172008175209	-0.12407452416663
C	-1.18397008260957	4.11121899787095	0.16654149094795
H	-2.09702087552420	4.63790306384229	0.38929713303336
C	-1.16921157055084	2.71855057929468	0.17191671293921
C	-2.44271967803970	2.01982703579513	0.46569006606971
C	-3.63087670782839	2.61349392108488	0.07183449055393
H	-3.59981214871438	3.46553503781897	-0.59048374906262
C	-4.88227054889825	2.15512830442396	0.51042001829761
H	-5.77770443093710	2.64378338522488	0.15489107923071
C	-4.95776921313983	1.13378421055011	1.41868959462363
H	-5.90609047101966	0.80914721161467	1.82397543780143
C	-3.78018124322105	0.47339197761426	1.83119609028238
C	-2.52766113468581	0.85419385303123	1.27491631263468
C	-3.79972141955769	-0.56878216004902	2.78007020264297
H	-4.74415919543625	-0.85748217335210	3.22160342116336
C	-2.63273190133829	-1.19829732727638	3.12915041022780
H	-2.60503592583130	-1.98192077135272	3.87055639373636
C	-1.46872504080542	-0.87144402002365	2.43290216877556
H	-0.56160905418149	-1.43299326944307	2.59530096908626



Model	ExpDec2
Equation	y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0
Plot	B
y0	7.54715 ± 0.77632
A1	248586.38921 ± 35257.00803
t1	420822.22447 ± 12725.30376
A2	13596.18865 ± 253.23801
t2	1.57437E6 ± 9727.76531
Reduced Chi-Sqr	327.83177
R-Square (COD)	0.99933
Adj. R-Square	0.99933

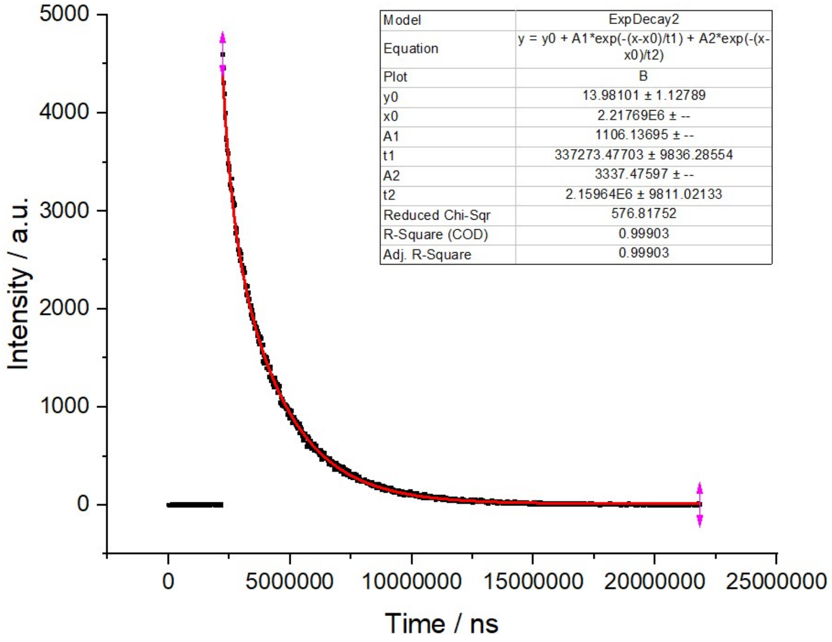
Fig. S10. Excited state lifetime fitting for ***rac*-Cr@SiO$_2$NPs** in aerated water solution in aerated medium (λ_{exc} = 375 nm).

a)



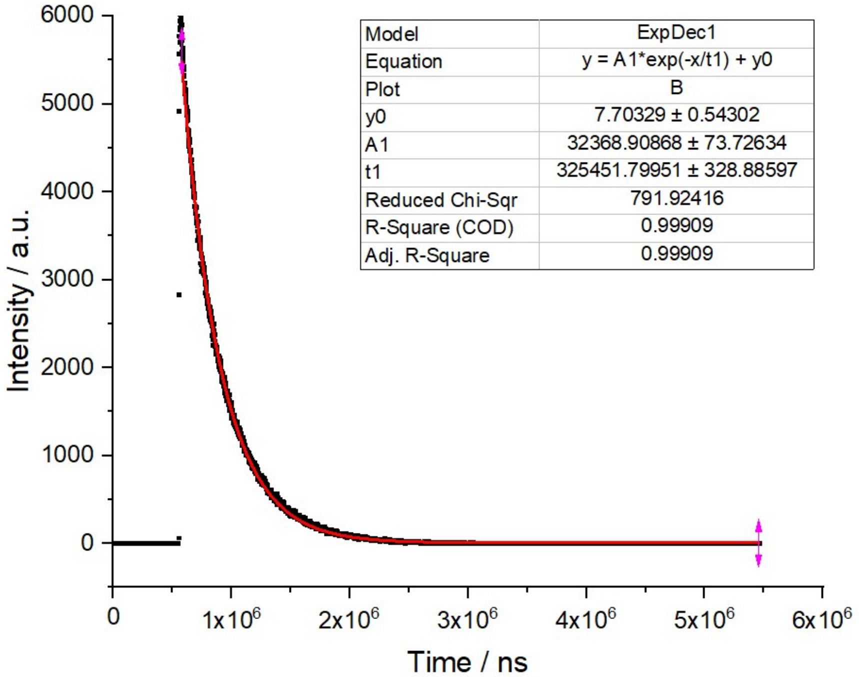
Model	ExpDec2
Equation	y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0
Plot	B
y0	4.18665 ± 0.70882
A1	981361.19886 ± 134089.33931
t1	336238.79388 ± 7501.18647
A2	13177.76146 ± 193.74971
t2	1.50964E6 ± 7804.47671
Reduced Chi-Sqr	288.34562
R-Square (COD)	0.99933
Adj. R-Square	0.99932

Fig. S11. Excited state lifetime fitting for ***rac*-Cr@SiO$_2$NPs** in solid state at room temperature (λ_{exc} = 375 nm).



Model	ExpDecay2
Equation	y = y0 + A1*exp(-(x-x0)/t1) + A2*exp(-(x-x0)/t2)
Plot	B
y0	13.98101 ± 1.12789
x0	2.21769E6 ± --
A1	1106.13695 ± --
t1	337273.47703 ± 9836.28554
A2	3337.47597 ± --
t2	2.15964E6 ± 9811.02133
Reduced Chi-Sqr	576.81752
R-Square (COD)	0.99903
Adj. R-Square	0.99903

Fig. S12. Excited state lifetime fitting for ***rac*-Cr@SiO$_2$NPs** in frozen solution H$_2$O/DMSO at 77 K (λ_{exc} = 375 nm).



Model	ExpDec1
Equation	y = A1*exp(-x/t1) + y0
Plot	B
y0	7.70329 ± 0.54302
A1	32368.90868 ± 73.72634
t1	325451.79951 ± 328.88597
Reduced Chi-Sqr	791.92416
R-Square (COD)	0.99909
Adj. R-Square	0.99909

Fig. S13. Excited state lifetime fitting for [Eu(tta)$_3$(phen-Si)] in dichloromethane at room temperature in aerated medium (λ_{exc} = 375 nm).

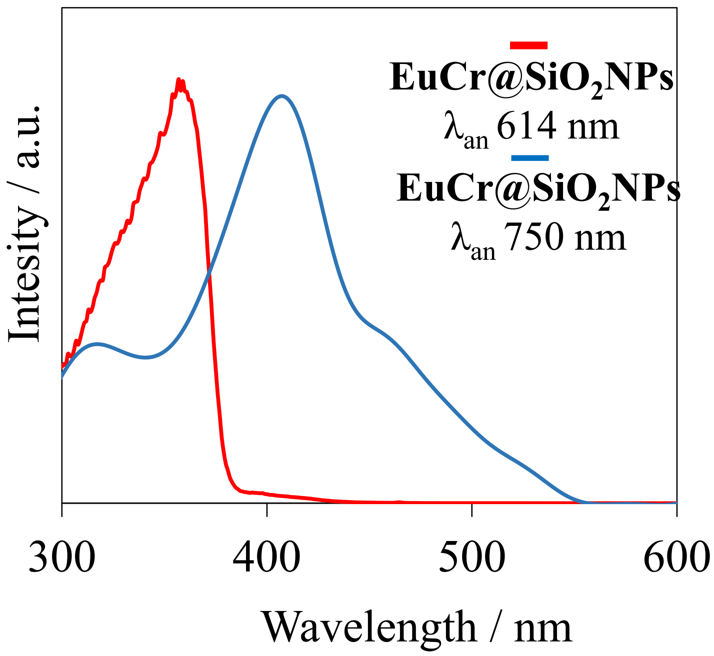


Fig. S14. Excitation spectra of the (*λλ/δδ*)-EuCr@SiO$_2$NPs at the maximum emission wavelength of 614 nm (Eu center) and 750 nm (Cr center).

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